Effect of disorder on the linear and nonlinear magnetic susceptibilities of two manganeseporphyrin-based magnets

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We analyze the effects of disorder on the magnetic properties of two manganeseporphyrins, [MnTPP][TCNE] · x(*o*-DCB) and [MnTPP][TCNE] · y(*o*-Xy) and (TPP=meso-tetraphenylporphyrinato, TCNE=tetracyanoethylene, *o*-Xy=*o*-xylene, *o*-DCB=*o*-dichlorobenzene, $x \leqslant 3$, $y \leqslant 1$). We present data for the in- and out-of-phase ac susceptibility and obtain the distribution of relaxation times using Cole–Cole analysis. The frequency dependence of the linear susceptibility suggests cluster glasslike behavior. The peak in the second harmonic of the ac susceptibility indicates the presence of a spontaneous magnetic moment. We propose that the unusual magnetic properties of these compounds reflect one-dimensional ferrimagnetic clusters interacting weakly through dipole-dipole interactions to form three-dimensional domains. © *1997 American Institute of Physics.* [S0021-8979(97)34408-9]

INTRODUCTION

The manganeseporphyrin-based magnets are quasione-dimensional electron transfer salts comprised of chains of alternating metalloporphyrin electron donors and cyanocarbon electron acceptors. The adjacent spins along these chains alternate, $S=2$ (donor) and $S=1/2$ (acceptor). This family of magnets provides an unusual opportunity for the study of magnetic ordering because it offers a wide range of controlling factors.[1]

The first member of the manganeseporphyrin family to be synthesized and studied was [MnTPP][TCNE].z(PhMe) (TPP=meso-tetraphenylporphyrinato, TCNE=tetracyano-ethylene, PhMe=toluene, $z \sim 2$).[2,3] [MnTPP][TCNE]·x(*o*-DCB), **1**, and [MnTPP][TCNE] ·y(*o*-Xy), **2**, are related compounds, obtained using different solvents, *o*-DCB and *o*-Xy (*o*-DCB=*o*-dichlorobenzene, *o*-Xy=*o*-xylene).[4] The maximum amount of solvent incorporated into the structure, as obtained from an x-ray structural determination, is 1 for *o*-Xy and 3 for *o*-DCB. The actual amount of solvent, as determined by thermogravimetric analysis, is, generally, less than the maximum values. Both compounds show one-dimensional (1D) ferrimagnetic behavior at high temperatures, with intrachain exchange of $J/k_B=-140$ K (for **1**) and $J/k_B=-82$ K (for **2**), determined from fits to a 1D model of alternating classical and quantum spins.[5] At temperatures $T<50$ K, the $\chi_{dc}T$ product was found to deviate above the prediction for 1D behavior, indicating ferromagnetic correlations between the chains.[5] Based on the absence of obvious interchain exchange pathways in these systems, we proposed[5] that the interchain interactions are dipolar in origin. Moreover, preliminary calculations of the critical temperature using estimates for the dipolar interaction strength, gave T_cs in qualitatively good agreement with the experimental values.[5] The low T limit of the in-phase ac susceptibility data ($T<4$ K) was found to be a nonzero constant, suggesting spin canting.[5]

EXPERIMENT

Polycrystalline powder samples of **1** and **2**, with $x \sim 2$ and $y \sim 1$ (determined from the room temperature magnetic moment and the low T saturation magnetization), were handled and weighed in an argon environment, and sealed in quartz tubes after being evacuated to 10^{-5} mbar, at room temperature. χ_{ac} was measured via the mutual inductance technique with a Lake Shore 7225 ac Susceptometer/dc Magnetometer in zero dc applied field and in the range $4<T<30$ K. A lock-in amplifier allowed phase sensitive detection such that both in (χ_1') and out-of-phase (χ_1'') linear susceptibilities, $\chi_1 = \chi_1' + i\chi_1''$ were measured under an ac field of 1 Oe and a wide range of frequencies ($5 \leqslant f \leqslant 10\,000$ Hz).

Harmonic susceptibilities χ_2 and χ_3 were obtained utilizing the $2f$ and $3f$ lock-in responses,[6,7] respectively, to an ac field ($H_{ac}=5$ Oe) with frequency f ($t=110$ and 1000 Hz). Both in- and out-of-phase components of the nonlinear susceptibilities were measured but in these cases only the magnitude of the response is reported.

RESULTS AND DISCUSSION

Typical frequency dependencies of the in-phase χ_1', and out-of-phase, χ_1'' linear ac susceptibilities of **1** and **2** are presented in Figs. 1 and 2, respectively. For both systems, the peak temperature of χ_1' increases and the peak height decreases with increasing frequency, indicative of glassy behavior.[8] For data shown here, values of the relative variation of the peak temperature per decade of frequency, $(\Delta T_p/T_p)/\Delta(\log f)=0.068$ and 0.038 for **1** and **2**, respectively, place these compounds between typical spin glasses and superparamagnets,[8] suggesting a picture of

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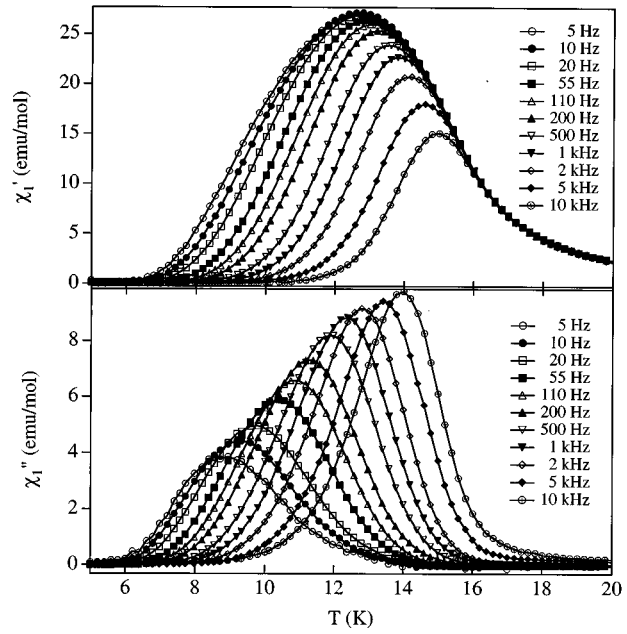

FIG. 1. Real and imaginary parts of χ_{ac} of **1** for $H_{ac}=1$ Oe ($H_{dc}=0$) and $5 \leqslant f \leqslant 10\,000$ Hz.

weakly interacting clusters. The value of $(\Delta T_p/T_p)/\Delta(\log f)$ varies with sample preparation, presumably due to change in solvent content.

The f dependence of χ_{ac} indicates long relaxation times. A detailed analysis of these relaxation times and their dependence on temperature is made using the phenomenological description of Cole and Cole.[9,10] Their formalism introduces a parameter $\alpha(0<\alpha<1)$, which determines the width of the distribution of relaxation times, $g(\ln \tau)$, around the median relaxation time, τ_c.

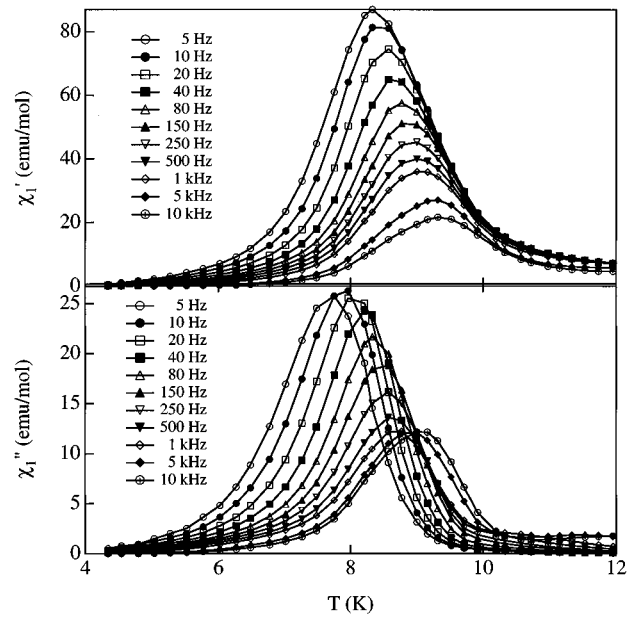

FIG. 2. Real and imaginary parts of χ_{ac} of **2** for $H_{ac}=1$ Oe ($H_{ac}=0$) and $5 \leqslant f \leqslant 10\,000$ Hz.

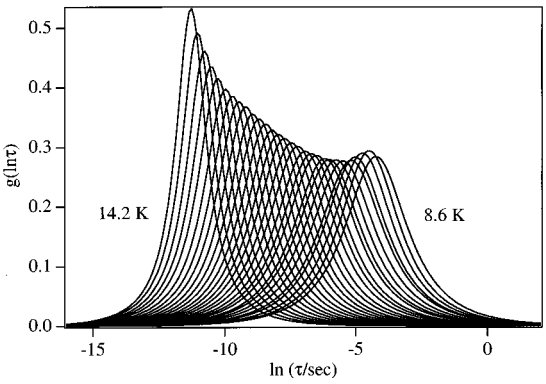

FIG. 3. Distribution of relaxation times of **1** for temperatures between 8.6 and 14.2 K, at intervals of 0.2 K, obtained by Cole–Cole analysis of the data of Fig. 1.

The distribution of relaxation times of **1**, obtained by fitting χ_1'' as a function of χ_1', at $8.6 \leqslant T \leqslant 14.2$ K (with α, τ_c, and the isothermal susceptibility as parameters) is plotted in Fig. 3. As T decreases, the median relaxation time increases from 10^{-5} s at 14.2 K to 10^{-2} s at 8.6 K, indicating the growth of the correlation length of the system of spins, as expected.[8] The width of the relaxation time distribution, however, has an unusual evolution with temperature. On cooling a canonical spin glass toward the freezing temperature and below, the parameter α is expected[8] to become larger, reflecting the fact that the distribution of cluster sizes broadens. For **1**, however, α increases with decreasing temperature, then levels off. Therefore, $\alpha(T)$ mimics that of a canonical spin glass above 10 K with a crossover to a weak T dependence reminiscent of a superparamagnet below 10 K.[10] We are led again to the picture of weakly interacting clusters.

For **2**, α and τ_c have many similarities to the case of **1**, the analysis being complicated by the presence of a weak second feature in the linear ac susceptibility data on the high temperature side of the peaks.[11]

The cluster glasslike behavior, suggested by the strong frequency dependence of the linear ac susceptibility data, is consistent, for both compounds, with the presence of irreversibilities in the field-cooled/zero-field-cooled magnetization data. Preliminary studies show field dependence of the bifurcation point between the field-cooled and the zero-field-cooled magnetization curves.[12]

The nonlinear ac susceptibility data (second and third harmonics) for **1** and **2**, Fig. 4, show along with the peak in the third harmonic, a peak in the second harmonic, indicating the presence of a spontaneous moment.[12]

The second harmonic can be observed only if there is a spontaneous magnetization because of the lack of inversion symmetry with respect to the applied field.[13] Unlike the case of a spin glass, where only odd harmonics are expected,[14] in the case of a ferromagnet, both even and odd harmonics should be present.[7]

A viable explanation of the glassy behavior in these compounds requires the identification of the sources

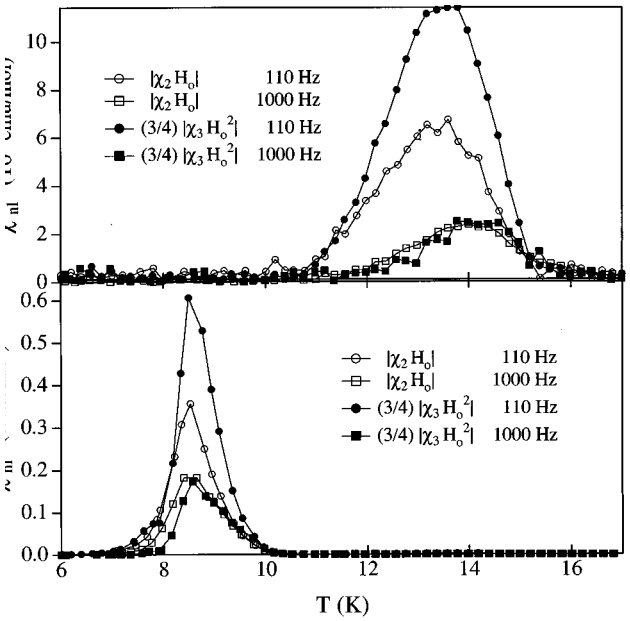

FIG. 4. Nonlinear susceptibilities $|\chi_{2,\mathrm{exp}}H_0|$ and $|3/4\chi_{3,\mathrm{exp}}H_0^2|$ measured at $2f$ and $3f$, respectively, in $H_{\mathrm{ac}}=5$ Oe ($H_{\mathrm{dc}}=0$) at $f=110$ and 1000 Hz, for (a) **1** and (b) **2**.

of disorder and frustration. The related compound [MnOEP][HCBD](OEP=octaethylporphyrinato, HCBD =hexacyanobutadiene) system, lacking solvent and structural disorder, does not show glassiness.[1] In contrast, based on structural data,[4] we propose that the sources of disorder in **1** and **2** are, most likely, solvent vacancies and/or solvent misorientations, and potentially different bonding patterns of the bridging TCNE molecule (which in turn may be related to the solvent vacancy). These different orientations of the TCNE molecule have been detected in a similar compound, $[\mathrm{MnTPP}][\mathrm{TCNE}]\cdot z(\mathrm{PhMe})$,[15] where it was found that about 15% of the TCNE molecules (''minor'' TCNE molecules) are rotated by 175° about the Mn–Mn axis. The structural disorder is likely to cause random intra and interchain interaction strengths, which constitute one of the necessary conditions for glassiness.

Given the strong intrachain antiferromagnetic interactions (~100 K), upon cooling these systems from room temperature, 1D ferrimagnetic correlations will build up one-dimensional clusters. Upon cooling further the single ion anisotropy (~1 K)[5] on the Mn, sites will start to play a role leading to preferred directions of the spins. Frustration may be caused by the weak interchain interaction (<0.01 K)[5] because of the long range and more complex dependence on spin orientation of the dipole-dipole interaction. The presence of the weak anisotropy and of the interchain dipole-dipole interaction leads to canting and the formation of 3D domains (consisting of quasialigned 1D clusters) that present a spontaneous magnetic moment. In analogy to the work of Thomson *et al.*[16] on the transverse freezing in frustrated Heisenberg systems, we speculate that within each domain there is a longitudinal component of the magnetic moment, while the transverse component probably averages to zero.

In conclusion, based on nonlinear harmonic susceptibilities and the frequency dependence of the linear ac susceptibility, we report, for two manganeseporphyrin compounds, similar transitions from a high temperature one-dimensional ferrimagnetic state to an unusual three-dimensional state with mixed weak ferromagnetic and cluster glasslike behavior. We propose that this unusual behavior is caused by disorder leading to the formation of one-dimensional clusters and three-dimensional domains. Within each domain, the clusters, made up of slightly canted antiferromagnetically coupled spins, tend to align due to the interchain dipolar interactions, causing a net magnetic moment.

ACKNOWLEDGMENTS

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[1] J. S. Miller and A. J. Epstein (unpublished); A. J. Epstein, C. M. Wynn, M. A. Gîrţu, W. B. Brinckerhoff, K.-I. Sugiura, and J. S. Miller (unpublished).
[2] J. S. Miller, J. C. Calabrese, R. S. McLean, and A. J. Epstein, Adv. Mater. **4**, 498 (1992).
[3] P. Zhou, B. G. Morin, A. J. Epstein, R. S. McLean, and J. S. Miller, J. Appl. Phys. **73**, 6569 (1993); W. B. Brinckerhoff, B. G. Morin, E. J. Brandon, J. S. Miller, and A. J. Epstein, *ibid.* **79**, 6147 (1996).
[4] K.-I. Sugiura, C. M. Wynn, M. A. Gîrţu, A. J. Epstein, A. M. Arif, and J. S. Miller (unpublished).
[5] C. M. Wynn, M. A. Gîrţu, W. B. Brinckerhoff, K.-I. Sugiura, J. S. Miller, and A. J. Epstein (unpublished); C. M. Wynn, M. A. Gîrţu, K.-I. Sugiura, E. J. Brandon, J. L. Manson, J. S. Miller, and A. J. Epstein (unpublished).
[6] T. Sato and Y. Miyako, J. Phys. Soc. Jpn. **51**, 1394 (1981).
[7] A. Chakravarty, R. Ranganathan, and C. Bansal, Solid State Commun. **82**, 591 (1992); S. Mukherjee, R. Ranganathan, and S. B. Roy Phys. Rev. B **50**, 1084 (1994).
[8] J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor and Francis, London, 1993).
[9] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941); C. Dekker, A. F. M. Arts, H. W. Wijn, A. J. van Duyneveldt, and J. A. Mydosh, Phys. Rev. B **40**, 11 243 (1989).
[10] D. Hüser, A. J. van Duyneveldt, G. J. Nieuwenhuys, and J. A. Mydosh, J. Phys. C **19**, 3697 (1986).
[11] M. A. Gîrţu, C. M. Wynn, J. S. Miller, and A. J. Epstein (unpublished).
[12] M. A. Gîrţu, C. M. Wynn, K.-I. Sugiura, J. S. Miller, and A. J. Epstein (unpublished).
[13] T. Hashimoto, A. Sato, and Y. Fujiwara, J. Phys. Soc. Jpn. **35**, 81 (1973).
[14] M. Suzuki, Prog. Theor. Phys. **58**, 1151 (1977).
[15] B. M. Burkhart, B. G. Morin, M. Sundaralingam, A. J. Epstein, J. C. Calabrese, and J. S. Miller (unpublished).
[16] J. R. Thomson, H. Guo, D. H. Ryan, M. J. Zuckermann, and M. Grant, Phys. Rev. B **45**, 3129 (1992).